Photodegradation of Polyimides. I. A Spectral, Viscometric, Chromatographic, and Weight Loss Investigation of Polyimides Based on a Hexafluorinated Dianhydride

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SYNOPSIS

The photodegradation of aromatic-dianhydride-based polyimide films in air with hexafluorinated groups in the dianhydride moiety is characterized by significant weight loss and chain cleavage. A conventional polyimide film based on pyromellitic dianhydride yields little decomposition under similar conditions of photolysis. Emission changes on photolysis of polyimide solutions demonstrate an efficient rearrangement to yield a highly fluorescent species which can be used as an effective tool for following the degradation process.

INTRODUCTION

Polyimides based on aromatic dianhydrides and diamines (or diisocyanates) continue to emerge as major materials for use in applications requiring polymers which are chemically resistant and thermally stable. In many cases polyimides are subjected to severe environments including exposure to ultraviolet radiation. This is particularly true for coatings applications where prolonged exposure to sunlight might be expected.

Polyimides which contain trifluoromethyl groups have been synthesized and characterized in a number of laboratories.[1-5] Polyimides based on the hexafluorinated dianhydride shown below (referred to hereafter as the 6F dianhydride) are especially attractive since they are soluble in a variety of common organic solvents and yet are still quite stable to thermal degradation. For example, the polymer films formed between 6F and 4,4'-oxydianiline (ODA) or 4,4'-methylenedianiline (MDA) show no appreciable decomposition to temperatures approaching 500°C:
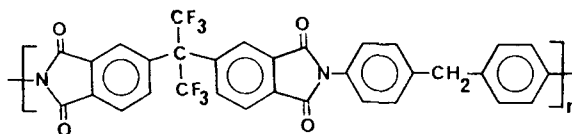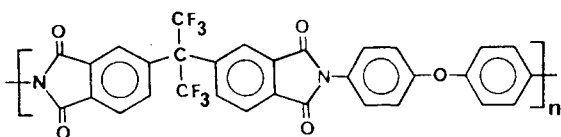
Despite the voluminous number of reports which detail the thermal properties of high temperature polyimides in general and the hexafluorinated polyimides specifically, one finds few reports[4,6-8] which describe the photochemically induced degradation of polyimides. When consideration is given to the number of applications and potential applications for polyimides which may require at least some exposure to light, it seems that a report on the effects of light radiation on the decomposition of polyimides is in order. In this first in a series of papers to be published on the photochemistry of polyimides, we will concentrate on the two polymers based on 6F and ODA (6F-ODA) and 6F and MDA (6F-MDA). The present study will be limited to an initial report of the spectroscopic, molecular weight, and weight

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loss changes resulting from photolysis with broad band radiation sources. The 6F polymers are well suited to an initial investigation of the photolysis of polyimides since they can be photolyzed both in solution and as films. In addition, since the exposed films remain soluble, they can be analyzed for
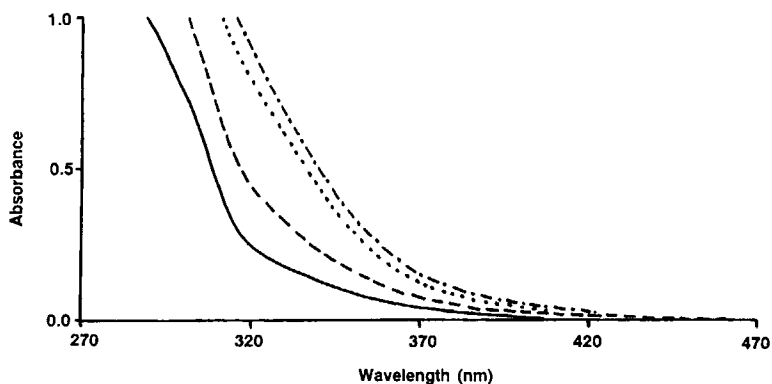

Figure 1   UV spectral change on photolysis of 0.089 mg/mL 6F-MDA in DMF (oxygen) with a Rayonet reactor (300 nm lamps): (a) 0 h (———); (b) 0.25 h (- - -); (c) 0.5 h (· · ·); (d) 1.0 h (- · - ·).
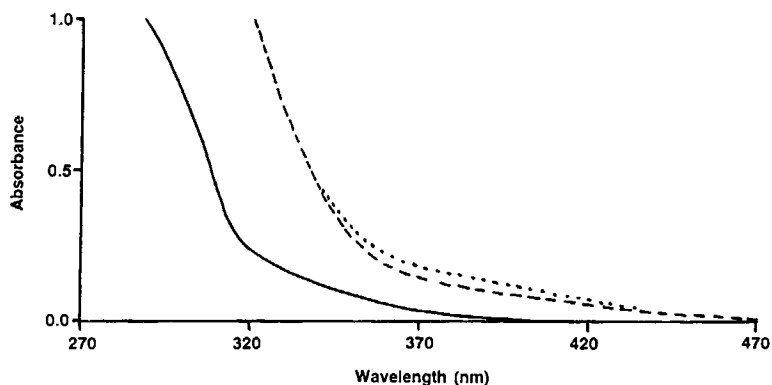

Figure 2   UV spectral change on photolysis of 0.089 mg/mL 6F-MDA in DMF (nitrogen) with a Rayonet reactor (300 nm lamps): (a) 0 h (———); (b) 0.5 h (- - -); (c) 1.0 h (· · ·).
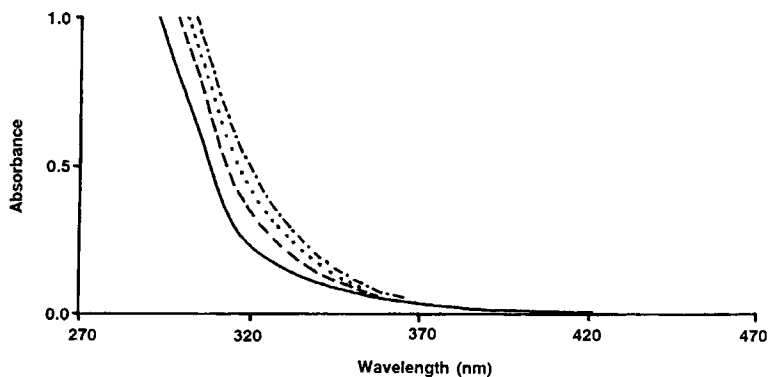

Figure 3   UV spectral change on photolysis of 0.085 mg/mL 6F-ODA in DMF (oxygen) with a Rayonet reactor (300 nm lamps): (a) 0 h (———); (b) 0.25 h (- - -); (c) 0.5 h (· · ·); (d) 1.0 h (- · - ·).
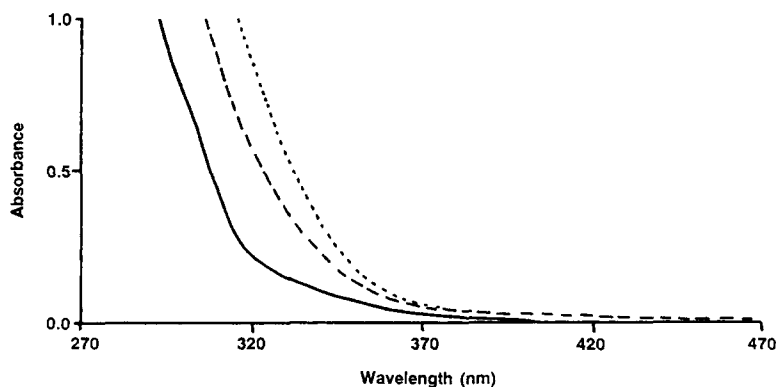
Figure 4   UV spectral change on photolysis of 0.085 mg/mL 6F-ODA in DMF (nitrogen) with a Rayonet reactor (300 nm lamps): (a) 0 h (———); (b) 0.5 h (– – –); (c) 1.0 h (· · ·).

changes in their molecular weight distribution profiles by viscometric and gel permeation chromatographic (GPC) techniques. Comparison with model compounds and identification of specific photoproducts is reserved for a separate publication.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (Aldrich) was recrystallized from methyl ethyl ketone (MEK) and vacuum sublimed prior to use. Polymer grade 2,2-bis(3',- 4'-dicarboxyphenyl)hexafluoropropane dianhydride (6F, Hoechst Celanese) was used without further purification. 4,4'-Oxydianiline (ODA, American Tokyo Kasei) was recrystallized from ethanol and sublimed under vacuum. 4,4'-Methylenedianiline (MDA, Aldrich) was vacuum distilled. Dimethylacetamide (DMAc, Aldrich) used as the solvent in the polymerizations and the viscometric analyses was dried over molecular sieve 4A and fractionally distilled under vacuum from calcium hydride. Spectroscopic grade dimethylforamide (DMF, American Burdick and Jackson) employed in the solution photolysis studies was used as received. Tetrahydrofuran (THF, J. T. Baker) used in the GPC was distilled under nitrogen from calcium hydride.
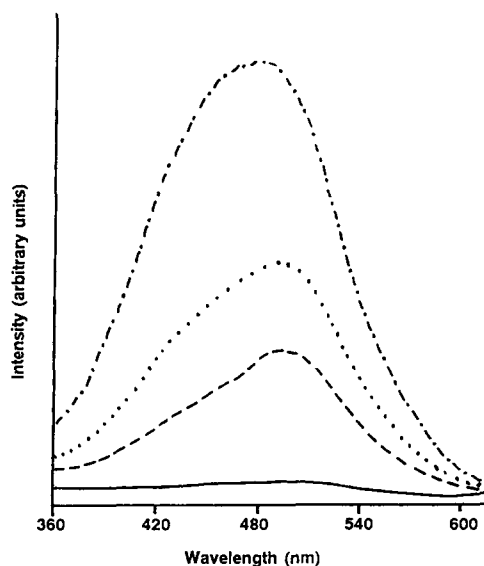

Figure 5   Fluorescence emission spectral change on photolysis of 0.089 mg/mL 6F-MDA in DMF (oxygen) with a Rayonet reactor (300 nm lamps): (a) 0 h (———); (b) 0.25 h (– – –); (c) 0.5 h (· · ·); (d) 1.0 h (–·–·).
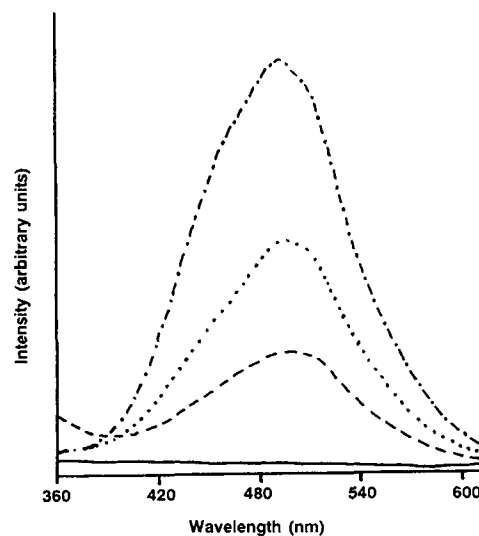

Figure 6   Fluorescence emission spectral change on photolysis of 0.085 mg/mL 6F-ODA in DMF (oxygen) with a Rayonet reactor (300 nm lamps): (a) 0 h (———); (b) 0.25 h (– – –); (c) 0.5 h (· · ·); (d) 1.0 h (–·–·).
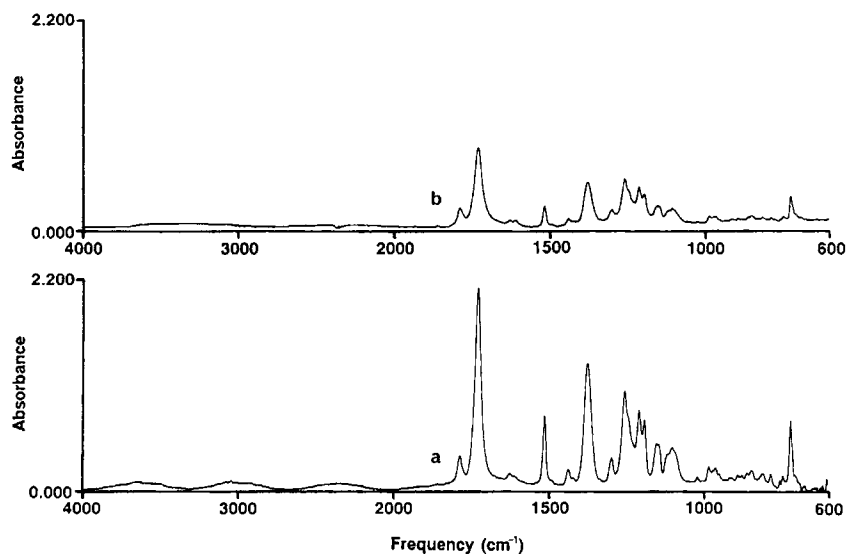
Figure 7 IR spectral change on photolysis of 6F-MDA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h; (b) 20 h.

Synthesis

In each case, the requisite diamine was dissolved in DMAc in a nitrogen-purged flask and an equimolar amount of the dianhydride was added. The reaction mixture contained 15 wt % solids and was stirred at room temperature for 8 h. The polyamic acid solution was poured onto soda lime glass plates and spread using a drawbar that produced a 4 mil thick wet film. The polyamic acid was thermally converted to polyimide by heating in a Blue M forced air oven. The temperature program used in the curing process involved 20 min at 60°C, 1 h at 100°C, 1 h at 200°C, and 1.5 h at 260°C. There was a ramp time between isothermal settings. The glass plates were placed in hot water to facilitate the removal of the polyimide films. FT-IR analyses of the films showed them to be essentially fully imidized. The characteristic imide bands[9] at 1780, 1720, 1370, and 720 cm^{-1} were seen in the IR spectra of the cured films. Inherent viscosities of the polyamic acids for 0.5 wt % solutions in DMAc at 35°C were as follows: PMDA–ODA, 1.19 dL/g; 6F-ODA, 0.69 dL/g; and 6F-MDA, 0.50 dL/g.
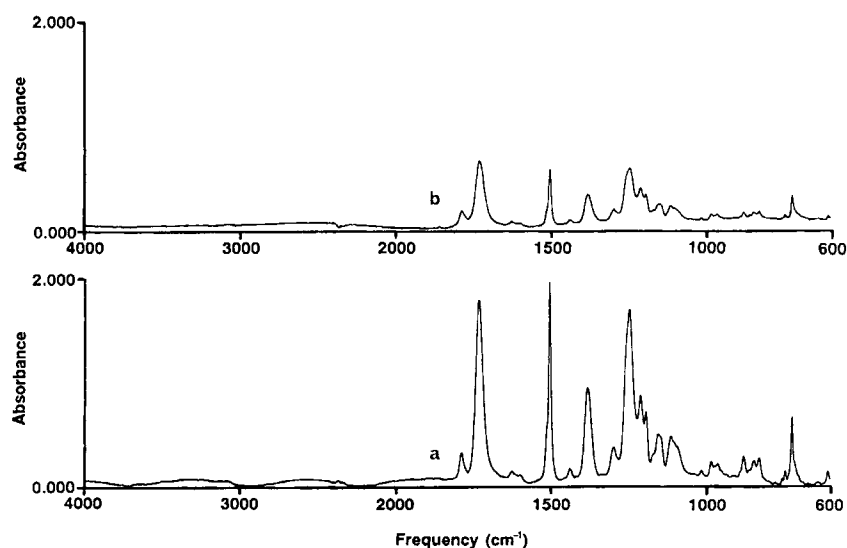

Figure 8 IR spectral change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h; (b) 20 h.
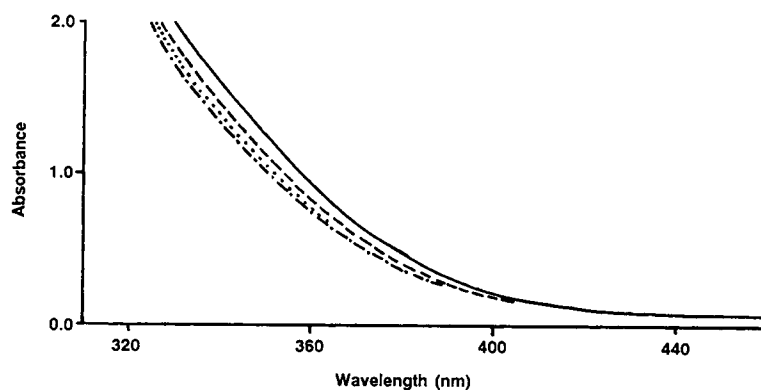
Figure 9 UV spectral change on photolysis of 6F-MDA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (———); (b) 4 h (– – –); (c) 12 h (· · ·); (d) 20 h (– · – ·).

Characterization

Infrared absorption spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrophotometer with 4 cm^{-1} resolution. A Perkin-Elmer Lambda 6 UV-VIS spectrophotometer with 1 nm resolution was used to record the UV absorption spectra.

The fluorescence emission spectra were determined from a Perkin-Elmer 650-10S fluorescence spectrophotometer. All samples were sparged with nitrogen before fluorescence measurements were taken. The fluorescence emission was measured at an angle of 90° to the excitation beam. Two-nanometer slit widths were used for both the excitation and emission monochromators.

The GPC analyses were carried out using the following conditions and equipment: solvent, THF; flow rate, 1.0 mL/min.; 100, 500, 10^4, and 10^5 Å Waters Ultrastryragel columns; Waters 410 differential refractometer. The calibration curve was based upon a series of polystyrene standards (Poly

sciences) possessing molecular weights of 1.86×10^6, 6.62×10^5, 7.48×10^4, 4.31×10^4, 1.68×10^4, 3.38×10^3, and 1.79×10^3. Molecular weights were determined from the peak maxima of the elution curves.

Inherent viscosity measurements were obtained using an Ostwald size 100 bore viscometer. Two-tenths weight percent solutions were prepared and equilibrated at 35°C.

Photolysis

The solution photolyses were carried out in a Rayonet RPR-100 photochemical reactor equipped with a full complement of sixteen 300 nm lamps. The solutions were placed in closed quartz test tubes and sparged with the desired gas before irradiation. A merry-go-round unit kept the center of the test tube 4.5 cm from the front of the lamps and allowed uniform irradiation of the samples.
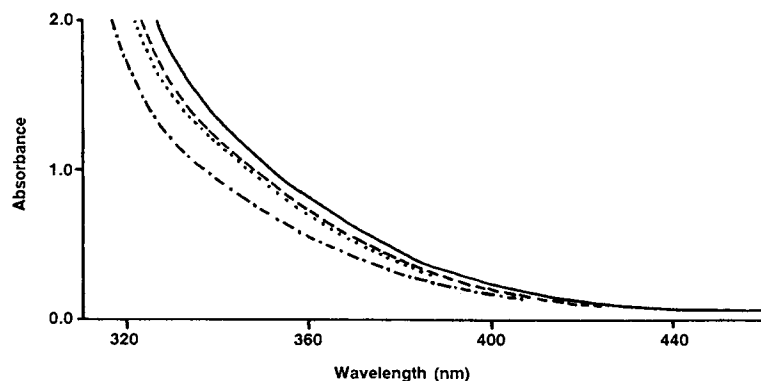

Figure 10 UV spectral change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h (———); (b) 4 h (– – –); (c) 12 h (· · ·); (d) 20 h (– · – ·).
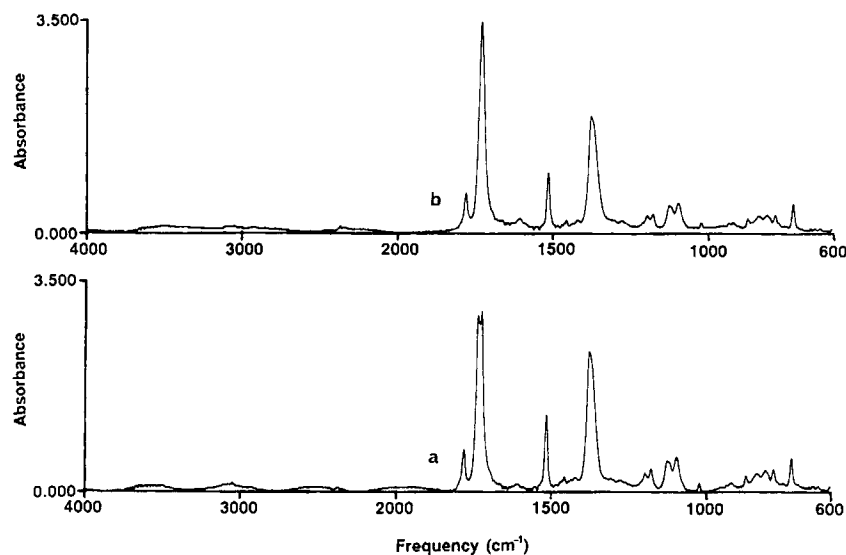
Figure 11   IR spectral change on photolysis of PMDA-MDA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h; (b) 36 h.

The film photolyses were conducted using the full arc of a 450 W Canrad-Hanovia medium pressure mercury lamp in air. The films were placed approximately 9 cm from the lamp.

RESULTS AND DISCUSSION

The Results and Discussion section will be divided into two parts: photolysis of polyimide solutions and photolysis of polyimide films. Although the two me-

dia represent different environments, it is possible to utilize results from both to provide a better overview of the basic polyimide photodecomposition process.

Solution Photolysis

Figures 1 and 2 show results for the changes in the UV absorption spectra of the 6F-MDA polymer as a result of photolysis of DMF solutions with a Rayonet Reactor (300 nm lamps used). Samples were oxygen (Fig. 1) and nitrogen (Fig. 2) degassed prior
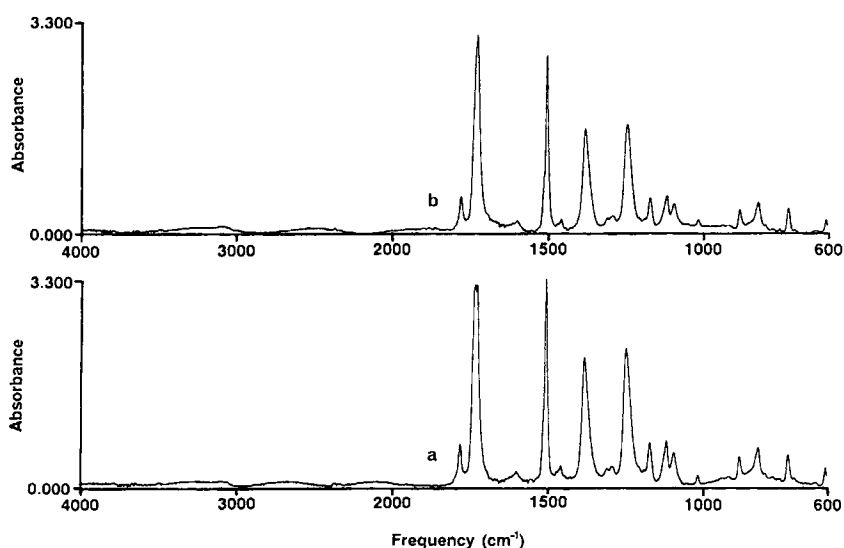

Figure 12   IR spectral change on photolysis of PMDA-ODA films in air using a medium pressure mercury lamp (unfiltered): (a) 0 h; (b) 36 h.
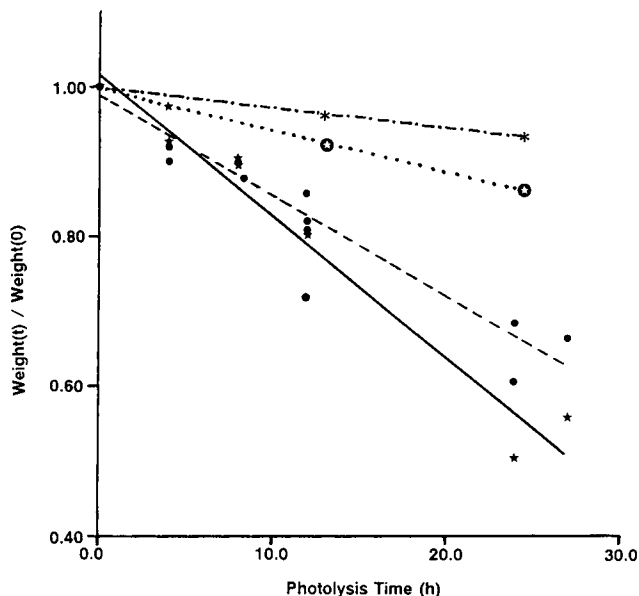
Figure 13   Weight change for photolysis of polyimide films in air using a medium pressure mercury lamp (unfiltered): (a) 6F-MDA (———); (b) 6F-ODA (– – –); (c) PMDA–MDA ($\cdot\,\cdot\,\cdot$); (d) PMDA–ODA, (– $\cdot$ – $\cdot$).

to and during irradiation. In both oxygen and nitrogen, there is a distinct red shift in the absorbance with increasing photolysis time. Perhaps the most striking aspect of these results is the large increase in absorbance for the nitrogen degassed solution. Similar results to those for the 6F-MDA polymers were obtained for the 6F-ODA system (Figs. 3 and

4). Apparently oxygen, at least under the conditions employed, serves to inhibit color formation in the photolyzed 6F-MDA and 6F-ODA polymers in DMF solution.

In a complementary study to the UV analysis, solutions of 6F-MDA and 6F-ODA polymer were photolyzed in oxygen and nitrogen saturated DMF solutions and their fluorescence emission spectra were recorded before and after photolysis. As shown in Figs. 5 and 6, prior to photolysis 6F-MDA and 6F-ODA there is no fluorescence from either polymer in solution. Following 0.25 h of photolysis, a very distinct broad emission is observed with a peak maximum around 490 nm (uncorrected). Additional photolysis results in a continued buildup in the peak at 490 nm with an accompanying shoulder appearing at about 460 nm. Similar results have been obtained for photolysis of a model compound. Although in this paper we will not attempt to give final assignments to the fluorescence peaks in Figures 5 and 6, it should be noted that such highly red shifted emission spectra with maxima between 460 and 500 nm are highly reminiscent of the reported fluorescence spectra of the substituted benzanilide chromophores which dominate the spectra of aramids such as poly(1,3-phenylene isophthalamide) and poly(1,4-phenylene terephthalamide).[10-13] Exact identification of the primary photochemical reactions of the basic benzimide group will be relegated to a separate publication which will include quantum yield studies for photolysis of model compounds. The results in
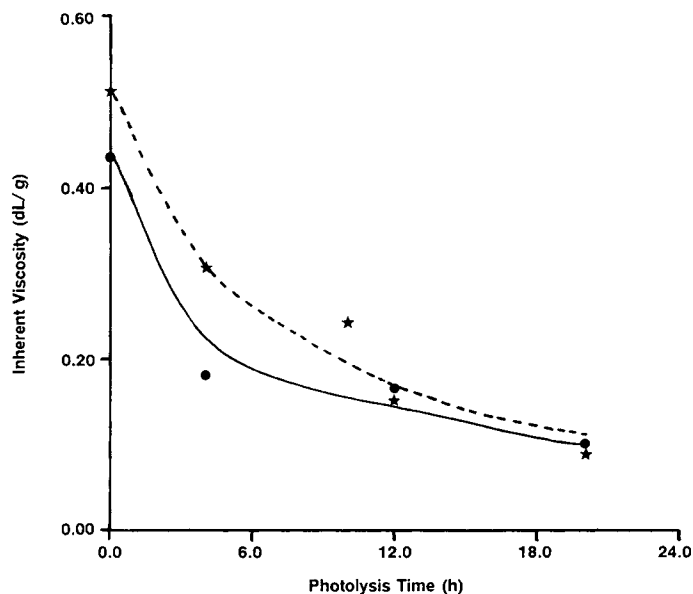

Figure 14   Inherent viscosity change on photolysis of polyimide films in air using a medium pressure mercury lamp (unfiltered): (a) 6F-MDA (———); (b) 6F-ODA (– – –).
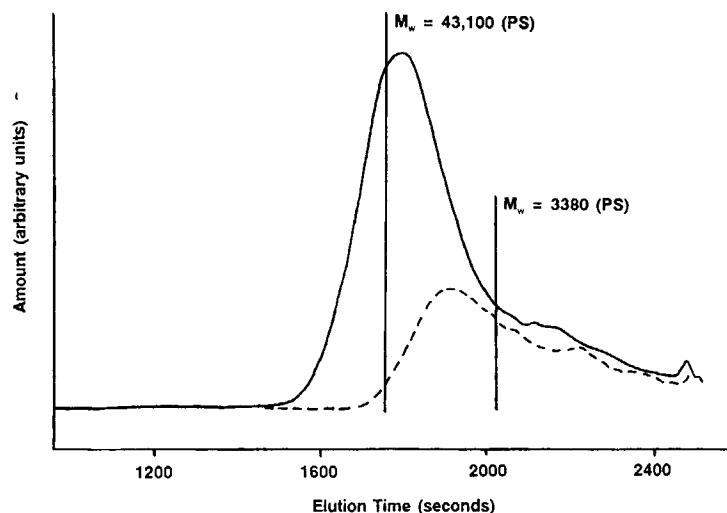
Figure 15   GPC curve change on photolysis of 6F-MDA films in air using a medium
pressure mercury lamp (unfiltered). The elution times for polystyrene standards are marked:
(a) 0 h (———); (b) 20 h (- - -).

Figures 1–6 are important for the present case since they vividly point out the labile nature of the polyimides based on 6F in solution and set the stage for the film photolysis investigations to follow.

Film Photolysis

Figures 7–10 show IR and UV spectra before and after photolysis of thin films of 6F-MDA and 6F-

ODA in air for 20 h with a medium pressure mercury lamp. For both polymers there is a significant and uniform decrease in all bands of the IR spectra accompanied by a blue shift in the UV spectra with no new peaks appearing above 350 nm. For comparison, the IR spectra of thin films of pyromellitic dianhydride (PMDA) and MDA or ODA photolyzed under similar conditions (Figs. 11 and 12) show much less change in the IR or UV spectra.
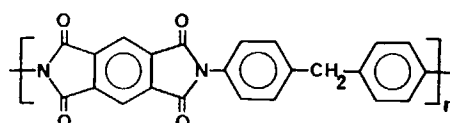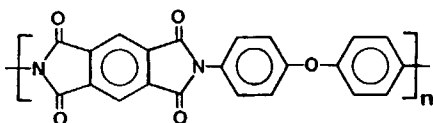
Apparently the bulkiness of the 6F group is instrumental in accelerating the photodecomposition of the polyimide film. Moreover, the uniform decrease in the IR spectra suggests that the films might be experiencing ablation under the conditions employed for photolysis. This presumption is borne out by the weight loss for the 6F-MDA and 6F-ODA films in air upon photolysis with a medium pressure mercury lamp (Fig. 13). Results for photolysis of PMDA–ODA and PMDA–MDA films are also shown in Figure 13. These data support the results of the IR and UV analysis and illustrate the photolability of the 6F polymers upon exposure in air to the full arc of a medium pressure mercury lamp.

Additional data which attests to the severe disruptive nature for the photodegradation process of the 6F polymers was obtained by analysis of the molecular weight changes as a function of photolysis (unfiltered medium pressure mercury lamp) of 6F-MDA and 6F-ODA films in air. Figure 14 shows a marked decrease in the inherent viscosity of 6F-MDA and 6F-ODA polymers photolyzed in the film state and subsequently dissolved in DMAc. In both cases, the decrease in the inherent viscosity is characterized by an initial drop by a factor of about 2 during the first 4 h of photolysis.

Regardless of photolysis time, the films remained completely soluble in DMAc indicating that no ap-
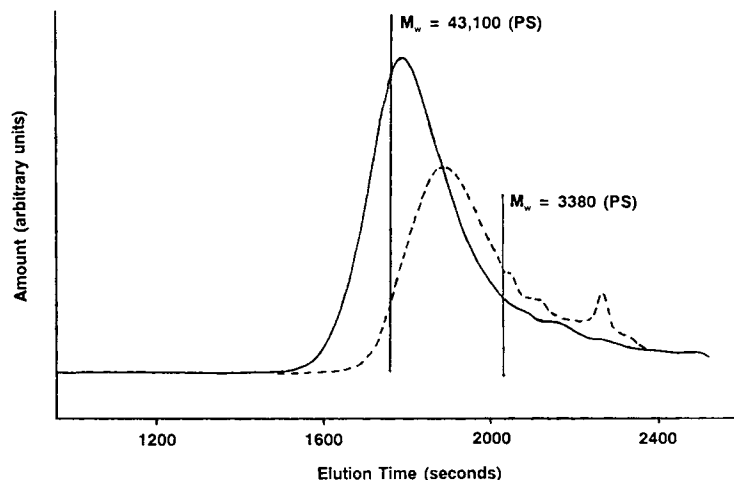
M$_w$ = 43,100 (PS)

M$_w$ = 3380 (PS)

Amount (arbitrary units)

1200   1600   2000   2400

Elution Time (seconds)

Figure 16   GPC curve change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered). The elution times for polystyrene standards are marked: (a) 0 h (———); (b) 20 h (– – –).

preciable crosslinking was taking place. Figures 15 and 16 show GPC traces of the 6F-MDA and 6F-ODA samples photolyzed in the film state for 20 h (unfiltered medium pressure mercury lamp). To illustrate pictorally the large change in molecular weight for the 6F polymers, Figure 17 shows a plot of the relative molecular weight (based on polystyrene) of the peak maxima (M_{MAX}) versus the photolysis time. The large drops in M_{MAX} after 4 h photolysis illustrate the initial rapid degradation of the polyimide film upon exposure to the unfiltered output of the mercury lamp and provides definitive evidence supporting a very efficient chain cleavage process in the photodegradation of the 6F polyimides.

CONCLUSIONS

This paper is the first in a series of studies on the effect of ultraviolet radiation on the degradation of polyimides. We have concentrated on a spectroscopic (UV, IR, fluorescence), chromatographic (GPC), and viscometric analysis of the changes induced in two fluorine containing polyimides (solution and film) upon exposure to broad band sources of ultraviolet light. The 6F-MDA and 6F-ODA polymers are highlighted in this first paper for two reasons: first and perhaps foremost because they are highly soluble in typical organic solvents and are thus amenable to investigation by GPC and viscometry. Second, the 6F polyimide films are unstable
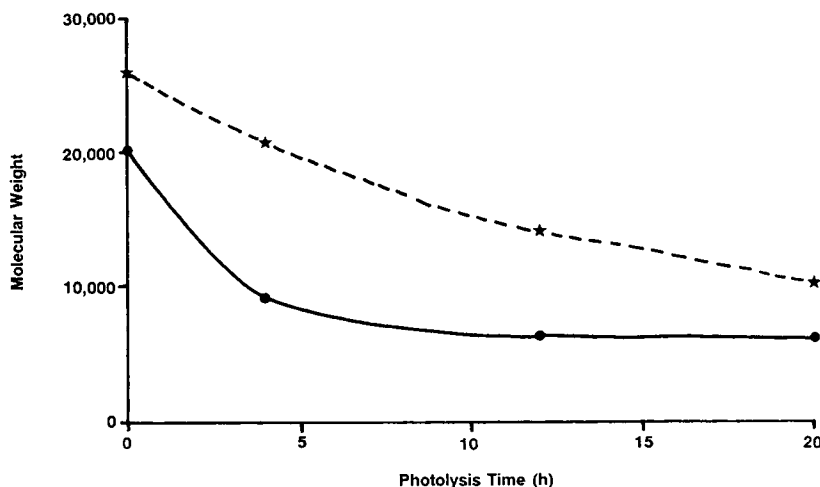
30,000

20,000

Molecular Weight

10,000

0

0   5   10   15   20

Photolysis Time (h)

Figure 17 M_{max} change on photolysis of polyimide films in air using a medium pressure mercury lamp (unfiltered): (a) 6F-MDA (———); (b) 6F-ODA (– – –).

photolytically in air and readily decompose under relatively (compared to most other polyimides) mild photolysis conditions, i.e., prolonged exposure for several days is not required to observe substantial changes. Specific results from this study are:

(a) 6F-based polyimides undergo facile and destructive (chain-breaking) changes upon photolysis with an unfiltered medium-pressure mercury lamp source.

(b) Photolysis of thin 6F polyimides films in air results in substantial loss in polymer weight.

(c) Weight loss of the 6F films in air is accompanied by substantial loss in molecular weight.

(d) Solution photolysis of 6F polymers results in the appearance of broad band fluorescence well above 400 nm.

Although we cannot as of yet define precisely the exact mechanism for photodegradation of the 6F polymers from the results presented in this paper, we can speculate on at least one of the primary photolysis reactions. One of the initial photochemical reactions is probably a carbon–nitrogen bond cleavage between the carbonyl carbon and the nitrogen in the imide linkage. In view of the complexity in assigning spectral peaks in photodegraded polymers to specific chromophores, we postpone specific assignments to a companion study of model compounds in progress.

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